

Ageing Characteristics of Al-Mg-(Ge,Si)-Cu Alloys

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Abstract. In order to elucidate some of the differences between Al-Mg-Si and Al-Mg-Ge alloys, a series of Al-Mg-Ge, Al-Mg-Si and Al-Mg-Ge-Si alloys, some of them containing Cu, are investigated by positron annihilation lifetime spectroscopy (PALS) during natural ageing (NA). Al-Mg-Ge alloys show qualitatively the same evolution of positron lifetime (LT) τ_{1C} with time as Al-Mg-Si alloys, namely an initial decrease, followed by a re-increase, after which τ_{1C} drops to an equilibrium value. However, for alloys with equal Mg contents, Ge notably retards the ageing kinetics as opposed to Si, pointing at effects of atomic size or solute/vacancy binding energies. The alloy with highest Mg and Si content shows the fastest natural ageing behavior, while the alloy with the highest Ge the slowest. Adding Cu to both Al-Mg-Ge and Al-Mg-Si alloys slows down the formation of clusters but promotes their growth.

Introduction

Al-Mg-Si alloys can be strengthened through precipitation hardening. Due to the practically unavoidable storage of Al-Mg-Si alloys at room temperature (RT) for a certain period before paint baking (which is equivalent to artificial ageing (AA) at ~ 180 °C for ~ 30 min), the increase in strength due to formation of β'' will be compromised. This is the so called ‘negative effect’ in these alloys and is known to be caused by solute clusters formed during natural ageing (NA). Cu addition to many industrial 6000 alloys can partly reduce the negative strength response through producing finer microstructures. On the other hand, after replacing Si by Ge, Al-Mg-Ge alloys show a similar precipitation behavior as Al-Mg-Si with the equilibrium phase Mg_2Ge [1]. Study of such alloys could provide more insight into the complex precipitation behavior of Al-Mg-Si, but except few investigations focused on the precipitate structure [2], little attention has been paid to these alloys in the past. Particularly, the clustering processes during NA have not yet been investigated. Therefore, by employing PALS the NA kinetics of Al-Mg-Ge alloys and the effect of Cu addition and Si substitution were studied.

Experiments

Samples. All investigated alloys were prepared from 99.99% purity Al by SINTEF. The chemical compositions were determined by means of X-ray microprobe, as listed in Table 1. Samples for PALS are $10 \times 10 \times 1$ mm³ large and were cut from homogenized and extruded bars. After mechanical grinding and cleaning, the Ge-free samples were solutionized at ~ 545 °C for 1 h in Ar atmosphere followed by ice water quenching, while for Ge-containing alloys 600 °C was applied. After this, the samples were cleaned, dried, assembled to the required sandwich geometry and placed into the sample holder.

Table 1: Composition of alloys. Other elements: Mn<0.004, Fe<0.007 and “-”<0.01 (all in at.%).

Designation	Si	Ge	Mg	Cu
G3	-	0.59	0.22	-
G11	-	0.14	0.25	-
G11Cu	-	0.13	0.24	0.11
GS3	0.31	0.20	0.24	-
GS11	0.18	0.04	0.44	-
GS11Cu	0.18	0.05	0.45	0.13
A2	0.83	-	0.41	-
A2Cu	0.87	-	0.50	0.12
A3	0.66	-	0.57	-
A3Cu	0.70	-	0.65	0.07
A11	0.40	-	0.84	-
A11Cu	0.45	-	0.86	0.11

between the 1.27 MeV γ photon emitted almost simultaneously with the positron and one of the 0.511 MeV annihilation γ photons that indicate the annihilation of a positron. Typical LT are 0.165 ns in bulk Al and 0.25 ns in a mono-vacancy in Al. Positrons can also be annihilate in solute clusters of a certain size formed during NA, with a LT depending on cluster properties.

Results and Discussion

Cu-containing alloys. Fig. 1(a) shows the evolution of τ_{IC} with NA time. It is similar to the previously investigated Al-Mg-Si alloys [4]. The initial LT (>0.23 ns) and stage I (<20 min) depend on the Mg and Si content: With higher Mg content and lower Si content, the initial value decreases as reported by [4], while the duration of stage I increases. For alloy A2 (Cu), stage I is very short and barely visible at room temperature due to its low Mg content. The exact origin of stage I is not known. During stage II, the LT drops to a minimum value (0.221–0.223 ns). Coherent clusters (~0.21 ns) enriched in Mg and Si, some possibly containing Cu, gradually form and compete with vacancy-related defects (~0.24 ns) in trapping positrons. The combination of both and the change of cluster composition leads to the observed LT evolution [4,5,6]. After this, the LT re-increases to a maximum within stage III. This stage occurs only if some 0.1% of Mg are present in the alloy [7] and is thought to be associated with the in-diffusion of Mg into the clusters in which the positrons annihilate [4,6]. Finally, the LT re-decreases through stage IV to a minimum value (<0.221 ns),

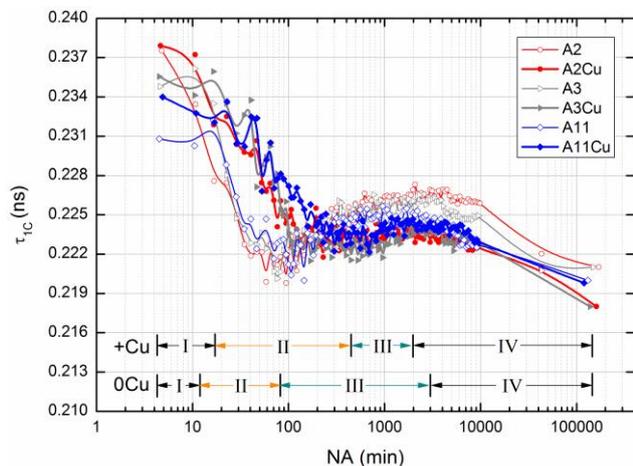


Figure 1: Positron LT evolution of Al-Mg-Si-(Cu) alloys during NA after quenching.

PALS. The NA kinetics of all the samples listed in Table 1 were measured using in-situ PALS in a ‘fast data acquisition’ mode [3]. The ‘sandwich’ containing both the samples and a ^{22}Na positron emitter (~15 μCi) was placed between two Philips XP2020Q detectors and arranged in co-linear geometry to ensure a high count rate. A 7-mm thick lead shield was put in front of the start detector to remove the influence from back-scattered γ quanta. The count rate was $\sim 600 \text{ s}^{-1}$ and a time resolution of 0.25 ns sufficient for one-component analysis. Spectra were fitted after subtracting the background and source contributions using the program LT9, yielding the positron LT τ_{IC} characterising the time difference

possibly due to coarsening or ordering of clusters. The various curves can be grouped into alloys without and with Cu. Alloys without Cu show a fast initial LT decrease with a minimum after about 1 h of NA and a much more pronounced increase can be observed after. In contrast, the times to reach a similar ageing state for Cu-containing alloys are ~ 8 times longer, indicating a retarded clustering kinetics due to Cu addition during stage II. However, stage III for alloys containing Cu is considerably shorter than in the Cu-free alloys, signifying that Cu can promote further development of these clusters after a certain NA time, see green arrows in Fig. 1.

Due to interactions between solutes and vacancies, solute clusters are formed via diffusion of solutes aided by vacancies. The rate of such a process depends on both the vacancy concentration and the diffusivity of the solute atom in the matrix. Due to the high solute-to-vacancy ratio after quenching (~ 100), only a small fraction of solutes is associated with monovacancies (the remainder is immobile) and becomes mobile as a complex if the binding is attractive. Otherwise, the vacancies will go to sinks after some random walk in the matrix. During diffusion of the complex, small vacancy/solute clusters can be formed rapidly, but the migration of these clusters becomes sluggish as they increase in size. Further formation of new clusters or the growth of existing ones eventually requires the liberation of vacancies from inside the clusters. However, the rate at which vacancies can escape and re-enter the matrix to transport more solutes depends on the binding energies between the vacancy and the cluster. Vacancies may be repeatedly trapped by and liberated from a cluster and an equilibrium between trapping and detrapping of vacancies by clusters is finally reached. As an example, if every cluster contains ~ 10 solute atoms on average [8], each vacancy would have to deliver at least 100 solute atoms in order to form ~ 10 clusters (the exact number of solutes to be transported by a vacancy depends on the fraction of atoms in clusters). Recently, a model has been proposed for the growth of solute clusters based on the binding energy E_b between a vacancy and a solute atom assuming that the probability for a vacancy to escape from a cluster scales with $\exp(-ncE_b)$, with n the number of atoms in that cluster and c a constant [9]. This directly implies that after a fast formation of clusters attributed to a high concentration of available vacancies, a slower growth rate of clusters is expected since a considerable amount of vacancies is increasingly being trapped by the growing clusters. Therefore, small clusters should be formed in a given time if strong binding existed between vacancy and solute, since one vacancy can only bring few solutes to form clusters [10]. In order to understand the phenomena caused by Cu addition, the binding energies listed in Table 2 between vacancy and solutes should be discussed:

Table 2: Solute radii r_s and vacancy-solute binding energies E_b (“+” stands for attractive, “-” for repulsive interaction, except V-Ge [11], other E_b are from [12])

	V-Mg	V-Si	V-Cu	V-Ge
r_s (Å)	1.50	1.10	1.35	1.25
E_b (eV)	0.04	0.05	0.09	60% higher than V-Si
f (s^{-1})	~ 190	~ 18200	~ 230	N/A

Many efforts have been made in the past to determine binding energies between a vacancy and various kinds of solutes. A collection of experimental values is available [13]. In calculations, the binding of V-Si was found to be attractive in all the studies e.g. [12,14,15], while V-Mg exhibits attractive binding for most cases, except the one reported by [11] who specifies a weak repulsive binding. In spite of few exceptions such as [14], the interaction between a vacancy and a Cu atom was found to be stronger or at least comparable to the ones of V-Mg and V-Si according to [13]. Our interpretation of the effect of Cu will be based on attractive and comparable binding energies between the vacancy and Mg/Si/Cu atoms, as the values shown in Table 2 obtained by a first-principle calculation [12]. For V-Ge we adopt the result by [11] that it is 60% stronger than the V-Si binding, based on first-principle density functional calculations.

Stage II: According to the binding energies summarized in Table 2, vacancies will bind with Cu atoms instead of assisting Mg-Si cluster formation and therefore reduce the migration of Mg and Si, i.e. slow down the rate of cluster formation. However, this simple mechanism would be small due to the relatively low concentration of Cu (0.1%). The jump frequency f of Cu at 20 °C was calculated according to [16] (using Eq (4) and values from Table 3&5 of [16]). The results are given in Table 2 together with the ones for Mg and Si. The calculated jump frequency of Cu equals $\sim 230 s^{-1}$ and lies therefore very close to the one for Mg. Once a vacancy is attached to Si, the vacancy can move with a high jump frequency to other vacancies/solutes to form small vacancy clusters [3], whereas for Cu or Mg, the jump frequency of a vacancy is two orders of magnitude smaller than for Si, i.e. vacancies are retained by Mg [17] or Cu atoms in an Al-Mg-Si-Cu alloy.

According to atom probe data [8], clustering during NA up to 2 weeks is dominated by Mg-Si and Mg-Si-Cu clusters consisting of 2 to 10 atoms on average. Cu incorporation into atomic clusters was also observed by [18]. Due to the attractive binding between Cu-V [12,13] and Cu-Mg [14] or even Cu-Si [8], the migration of V-Mg or V-Si complexes necessary for the formation of binary Mg-Si clusters could be notably slowed down if a Cu atom was located in its vicinity [19], which is very likely since the distances among vacancies and solutes/clusters are small in the initial stage of cluster formation. More important, if each vacancy has to transport Mg and Si atoms to the cluster repeatedly, the influence of Cu on clustering would be larger than expected from its low concentration because every time a vacancy detaches from a cluster, it can be temporarily trapped by a Cu atom with a certain probability. These probabilities will further increase when the matrix is depleted of Mg and Si atoms due to clustering. The total probability will be the sum of the individual probabilities. The formation of ternary clusters containing Cu could be even slower due to the low jump frequency of V-Cu, and since detrapping of a vacancy from clusters containing both Mg and Cu could become increasingly difficult, again as a result of the interaction between vacancies and solute atoms. Under such circumstances, smaller clusters should be formed in the presence of Cu. This coincides with the observed slightly higher positron LT at the end of stage II, since it is cluster growth that reduces the LT in stage II.

Retardation of clustering during NA has been observed by many authors and is consistent with the PALS observations of this study. For example, a reduced rate of NA caused by Cu addition to Al-Mg-Si alloys was found by TEM [19]. Electrical resistivity measurements suggested a reduction of the migration rate of solute atoms by a factor of 10 due to Cu addition [20]. Using the same Cu-containing Al-Mg-Si alloys as in this work, [18] reported a slower increase of hardness during the first 2000 min of NA. In analogy to our case it was shown that due to stronger interactions of vacancies with Sn than with Cu, Cu clustering or GP zone formation was suppressed in an Al-Cu-Sn alloy, because the number of vacancies enabling Cu diffusion is reduced [21].

Stage III: Beside the Mg-Si and Mg-Si-Cu clusters discussed above, considerable amounts of Cu-Mg and Cu-Si clusters (3-10 atoms) were also identified by [8] after 2 hours of NA. Due to the presence of Cu, the total number of clusters is 1.78 times higher than the number of Mg-Si clusters. In another atom probe study, adding Cu led to an increase in the total number of clusters by a factor of ~ 1.26 [22]. If smaller but more densely distributed clusters are formed in the Cu-containing alloys during stage II, then Mg atoms, which dominantly contribute to the further growth of clusters during stage III, would benefit from the shorter average distance to the clusters. The time t for a Mg atom to diffuse to a cluster scales with the average distance x squared, and this distance scales with the number density n to the power of $-1/3$. Thus $t \sim n^{-2/3}$. Taking the mean of the two experimental values for the increase of n , 1.52, the migration time for a Mg atom to reach a cluster will be reduced to 0.76 the original value. This agrees qualitatively with observed shortening of stage III in Fig. 1 from 3000 min to 2000 min. After 1 week of NA, a higher number density of clusters was identified by atom probe in the Cu-containing alloys than the alloy with equal amount of Mg and Si but without Cu [22]. It was suggested that nucleation and growth of solute clusters is aided by Cu addition during NA. In the same work, it was also found that in the presence of Cu, the Mg/Si ratio in clusters became higher, which might be another indication of an attractive binding between Mg and Cu. Furthermore, our observations agree with hardness measurements [18] that reflect the property of Cu to slow down early clustering and accelerate later stages.

Ge-containing alloys. Al-Mg-Ge and Al-Mg-Si alloys show largely the same evolution of LT during stages II, III and IV, but stage I was not observed and the initial LT is no more related to the Mg content of the Ge containing alloys, see Fig. 2(a). Therefore, the interplay between Mg and Ge on the one hand and Mg and Si on the other is qualitatively the same, but the action of Ge and Si differ in that at a given Mg content, more Si increases the rate of LT decrease in stage II, whereas more Ge delays it. For example, the highest Ge content in alloy G3 leads to the longest transition times t_{II-III} and t_{III-IV} between stages II to III and III to IV, respectively, while for the alloy G11 with much less Ge, both transition times are markedly reduced. On the other hand, the ageing kinetics can be further accelerated by substituting certain amounts of Ge by Si while keeping the Mg content

nearly constant, see alloy GS3, thus suggesting a kind of compensation between the effects of Si and Ge. Finally, the fastest transition times were obtained in alloy GS11, which contains the highest amount of Mg and some Si, but the lowest Ge content, see Fig. 2(a). The effect of Cu in Al-Mg-Ge alloys for low Ge and Mg contents is the same as for Al-Mg-Si alloys (compare G11 and G11Cu), namely Cu retards the decrease of LT and leads to a less pronounced increase after the minimum.

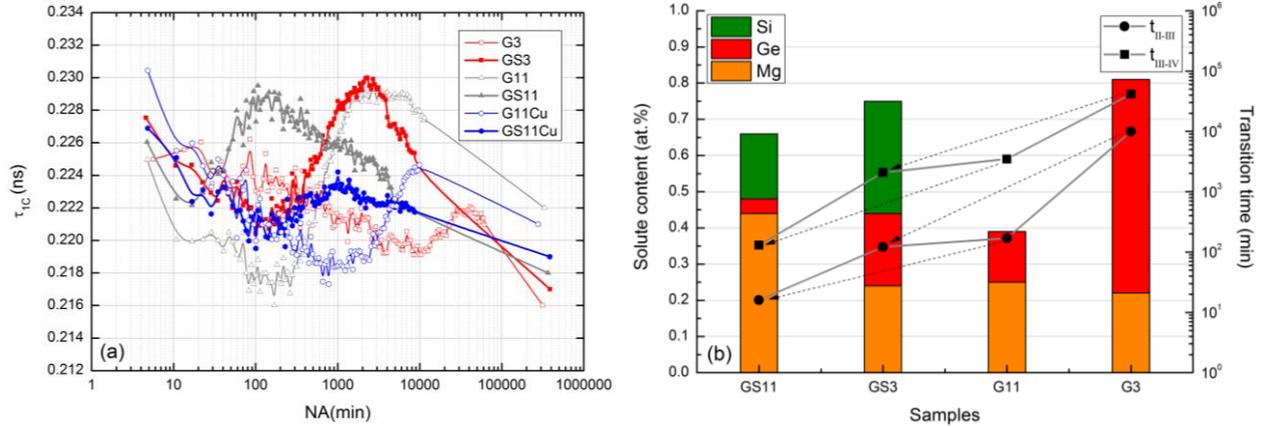


Figure 2: (a) Positron LT evolution in Al-Mg-(Ge,Si)-Cu alloys during NA; (b) Dependence of transition time t_{II-III} for stage II to III and t_{III-IV} for stage III to IV on sample composition.

The diffusivity of a solute atom depends on various factors such as atomic size, excess valence and solubility of the solute in Al [16]. Due to our lack of knowledge about Ge, the calculation of the corresponding jump frequency could not be performed. If we assume a slow migration rate of V-Ge and associate this with the sluggish jump frequency of Mg, the extremely slow ageing kinetics of G3 alloy appears plausible. The rate of clustering in Al-Mg-Si alloys is much faster than in Al-Mg-Ge alloys, since Si atoms can rapidly diffuse towards Mg and form clusters although the jump frequency of Mg is low.

A correlation between the binding energy and solute size has been proposed, i.e. strong binding occurs as a rule (with exceptions such as for Mg) between a vacancy and a large solute atom [11]. Hence, a higher binding energy of Ge-V is expected than Si-V owing to the larger atomic radius of Ge, see Table 2. [23] investigated Al-10%Zn-0.12%Ge and Al-10%Zn-0.1%Si (in wt.%) alloys isothermally by means of electrical resistivity measurements. Retarded ageing kinetics were observed in the Ge-containing alloys at various temperatures ranging from 0 °C to 40 °C and a higher binding energy of Ge-V than Si-V was determined. Such a tendency confirms the binding energies for V-Ge and V-Si listed in Table 2. In such a case, the clustering processes in the alloys containing certain amount of Ge should be retarded, due to the combined effects of the low mobility of V-Ge complexes as well as the reduced number of available vacancies for the transport of Mg and Si atoms, in a similar manner to Cu-containing alloys.

Summary

An experimental study on the natural ageing characteristics of Al-Mg-(Ge,Si)-Cu alloys by means of positron annihilation lifetime spectroscopy showed that:

1. The evolution of positron LT follows the same pattern for all the alloys studied.
2. Ge notably retards the natural ageing kinetics compared to Si. The alloy with the highest Mg and Si content shows the fastest natural ageing.
3. A similar effect was observed for Cu in both Al-Mg-Ge and Al-Mg-Si alloys: Cu first slows down the formation of clusters but it later promotes their subsequent growth. Possible reasons could be related to the interactions between vacancies and solutes or solute clusters.

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